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Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

Sub-Committee of Experts on the Transport of Dangerous Goods

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Item 6 (b) of the provisional agenda
Transport of gases: miscellaneous

Packing instructions P200 and P206 for collective entries

Transmitted by the expert from Germany[1]

Introduction

1. At its forty-forth session, the Sub-Committee considered a proposal to amend packing instructions P200 and P206 and to include instructions how to calculate the filling ratio and test pressure when a liquid phase of a fluid is charged with a compressed gas (see ST/SG/AG.10/C.3/2013/41). Some experts considered that this would be better addressed through standards and that it was not desirable to include such detailed calculation formulae in regulations which should contain the essential requirements. Others supported the proposal in general and provided some editorial remarks.

2. The expert of Germany is still of the opinion that an amendment of P 200 and P 206 is necessary. There are no appropriate standards to be referenced in the provisions, therefore the instructions have to be included in the Model Regulations.

3. For the collective entries

- UN 1058 "LIQUEFIED GASES, non-flammable, charged with nitrogen, carbon dioxide or air"
- UN 3157, 3160, 3161, 3162, 3163, 3307, 3308, 3309, 3310 "LIQUEFIED GAS, XXXX, N.O.S.",

[1] In accordance with the programme of work of the Sub-Committee for 2013–2014 approved by the Committee at its sixth session (see ST/SG/AC.10/C.3/84, para. 86 and ST/SG/AC.10/40, para. 14).

- UN 3500, 3501, 3502, 3503, 3504, 3505 "CHEMICAL UNDER PRESSURE, XXXX, N.O.S."

P200 (3) or P206 (3), respectively, is applicable for the calculation of the filling ratio and the test pressure.

4. For cases where a liquid phase of a fluid is charged with a compressed gas, the above packing instructions do not include instructions on how to calculate the filling ratio and test pressure. In these cases, both components – the liquid phase and the compressed gas – have to be taken into consideration in the calculation of the internal pressure in the pressure receptacle.

This is shown in Figure 1:

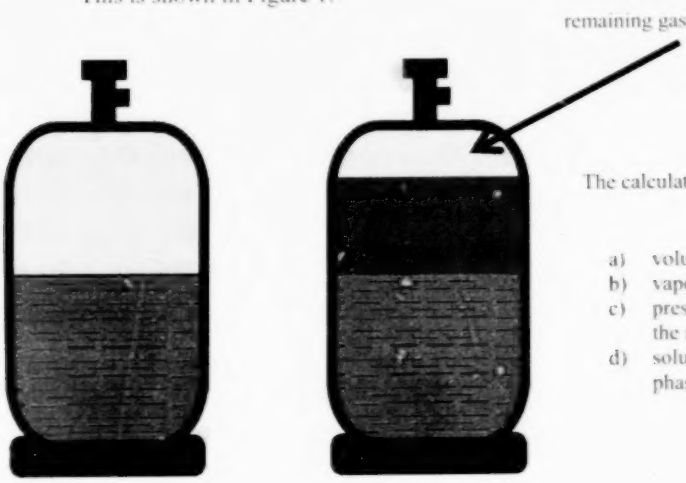
remaining gas volume
The calculation has to consider the following:
a) volumetric expansion of the liquid phase;
b) vapour pressure at 65 °C;
c) pressure of the compressed gas at 65 °C in the reduced volume;
d) solubility of the compressed gas in the liquid phase.
T = 15 °C
T = 65 °C

Fig. 1: Schematic presentation of the volumetric expansion for the calculation of the internal pressure in pressure receptacles containing liquid phases and compressed gas

5. If only the compressed gas is considered in accordance with P200 (3) (a), this results in calculated pressures which are too low and not acceptable from the point of view of safety. If only the vapour pressure of the liquefied component at 65 °C is considered in accordance with P200 (3) (c) and/or P206 (3), this also result in calculated pressures which are too low and not acceptable from the point of view of safety.

6. A complete calculation formula is not given in P200 and P206. Experimental values are often also not available. A calculation on the basis of the existing provisions may lead test pressures that are too low, this is illustrated by the following example:

Example

Gas for use in hot air balloon:

UN 1978 propane, charged with 5 bar(abs) nitrogen

According to existing P 200:

Filling ratio (P200 (c)) = (0.0032 x BP – 0.24) x dl = (0.0032 x 231 – 0.24)x 0.5809 = **0,29 kg/l**

Test pressure (P200 (c)) = vapour pressure at 65 °C – 1 bar = (23.43 – 1) bar = **22.4 bar**

According to proposed amendment P200 (see para6):

(a) Vapour pressure and partial pressure at filling temperature /1/vapour pressure propane (15 °C) = 7.315 bar(abs)partial pressure nitrogen (15 °C) = 5 bar(abs)

(b) Volumetric expansion of liquid phase from 15 °C to 65 °C /1/filling ratio = 0,29 kg/l, liquid density (15 °C) = 0.5075 kg/l, liquid density (65 °C) = 0.4163 kg/lvolumetric expansion of liquid phase: From 0.571 l (15 °C) to 0.6966 l (65 °C), remaining gas volume in the gas cylinder: 1-0.571 = 0.429 (15 °C), 1-0.6966 (65 °C) = 0.303 (65 °C)

(c) Partial pressure of nitrogen at 65 °CpN2 = 5 x 338.15/288.15 x 0.429/0.303 = 8.3 bar(abs)

(d) Vapour pressure at 65 °C /1/pv (65 °C) = 23,43 bar(abs)

(e) Total pressure at 65 °Cpt (65 °C) = 23,43 bar + 8,3 bar = 31.73 bar(abs)

7. A similar approach to calculating test pressures (design pressure) taking into account both the compressed gas and the liquid phase for tanks is given under 6.7.2.1 and 6.7.3.1.

Proposal

8. The following amendments to P200 and P206 are proposed (amended text compared to document 2013/41 is printed underlined)

Insert a new paragraph (e) in P200 (3):

"(e) For liquefied gases charged with compressed gases, both components – the liquid phase and the compressed gas – have to be taken into consideration in the calculation of the internal pressure in the pressure receptacle.

The maximum mass of contents per litre of water capacity shall equal 0.95 times the density of the liquid phase at 50 °C; in addition, the liquid phase shall not completely fill the pressure receptacle at any temperature up to 60 °C.

When filled, the internal pressure at 65 °C shall not exceed the test pressure of the pressure receptacles. The vapour pressures and volumetric expansions of all substances in the pressure receptacles shall be considered. When experimental data is not available, the following steps shall be carried out:

(a) Calculation of the vapour pressure of the liquid component and of the partial pressure of the compressed gas at 15 °C (filling temperature);

(b) Calculation of the volumetric expansion of the liquid phase resulting from the heating from 15 °C to 65 °C and calculation of the remaining volume for the gaseous phase;

(c) Calculation of the partial pressure of the compressed gas at 65 °C considering the volumetric expansion of the liquid phase;

(d) Calculation of the vapour pressure of the liquid component at 65 °C;

(e) The total pressure is the sum of the vapour pressure of the liquid component and the partial pressure of the compressed gas at 65 °C;

(f) Consideration of the solubility of the compressed gas at 65 °C in the liquid phase;

The test pressure of the pressure receptacle shall not be less than the calculated total pressure minus 100 kPa (1bar).

If the solubility of the compressed gas in the liquid component is not known for the calculation, the test pressure can be calculated without taking the gas solubility (paragraph (f)) into account.

At the end of P206 (3), add the following paragraph:

For liquids charged with a compressed gas both components – the liquid phase and the compressed gas – have to be taken into consideration in the calculation of the internal pressure in the pressure receptacle. When experimental data is not available, the following steps shall be carried out:

(a) Calculation of the vapour pressure of the liquid component and of the partial pressure of the compressed gas at 15 °C (filling temperature);

(b) Calculation of the volumetric expansion of the liquid phase resulting from the heating from 15 °C to 65 °C and calculation of the remaining volume for the gaseous phase;

(c) Calculation of the partial pressure of the compressed gas at 65 °C considering the volumetric expansion of the liquid phase;

(d) Calculation of the vapour pressure of the liquid component at 65 °C;

(e) The total pressure is the sum of the vapour pressure of the liquid component and the partial pressure of the compressed gas at 65 °C;

(f) Consideration of the solubility of the compressed gas at 65 °C in the liquid phase.

The test pressure of the cylinders or pressure drums shall not be less than the calculated total pressure minus 100 kPa (1bar).

If the solubility of the compressed gas in the liquid component is not known for the calculation, the test pressure can be calculated without taking the gas solubility (paragraph (f)) into account.